

flow softening which a small-scale, short-time experiment unfortunately cannot disclose. (1) Difficulty of distribution in large units to obtain uniformity of contact in upflow; (2) increased attrition and loss of zeolite with upflow as compared with downflow; (3) increased danger of gravel hills with upflow; and (4) upflow provides no filtration effect; in softening filtered water this would not seem to be important.

Future runs will be made to determine whether the zeolite can be made to show greater capacity between regenerations

and whether consistent results during six to ten runs and regenerations for each set of constant conditions can be obtained. Salt-saving methods may also be investigated.

Acknowledgment

The authors wish to acknowledge valuable assistance and suggestions received from W. J. Hughes and A. S. Behrman, of the International Filter Company, and from S. B. Applebaum, of the Permutit Company.

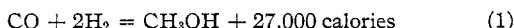
A Study of the Synthesis of Methanol¹

Abstract

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THE synthesis of methanol consists in directly combining carbon monoxide with hydrogen at high pressure in accordance with the equation



This reaction liberates about 843 gram-calories per gram of alcohol produced and transforms into the liquid form 82.7 per cent of the heat content of the reacting gases, the remaining 17.3 per cent being dissipated in the form of heat. In a gas mixture having the theoretical composition of carbon monoxide and hydrogen in the ratio 1:2, the percentage, x , of the carbon monoxide converted into methanol at equilibrium is defined approximately by Nernst's formula,

$$\text{Log} \frac{(1-x)^3}{x(3-2x)^2} = \frac{-27,000}{4.571 T} + 3.5 \log T + 2.9974 - 2 \log P \quad (2)$$

where T represents the absolute temperature and P the pressure in atmospheres, common logarithms being used. For another ratio of hydrogen to carbon monoxide in the initial gas mixture, the conversion may be expressed as a function of x by the law of mass action. For instance, when the initial gas mixture has the composition $\text{CO} + 5\text{H}_2$, the percentage of carbon monoxide going to methanol, y , is defined as a function of x by the equation

$$\frac{(1-y)(5-2y)^2}{4y(3-y)^2} = \frac{4(1-x)^3}{x(3-2x)^2} \quad (3)$$

The values of x and y as calculated from equations (2) and (3) are plotted as functions of temperature in Figure 1, showing that only relatively low pressures are required to effect the alcohol synthesis as long as the temperature does not exceed 300° C.

In the synthesis of methanol, as in any other reaction between gases in contact with a solid catalyst, the rate of product formation is of utmost importance from the point of view of industrial feasibility. This rate is best expressed as the amount of alcohol which can be obtained per unit time per unit volume of catalyst, and is a function of the following variables: (1) the nature of the catalyst used, (2) the chemical composition of the gas mixture at the point of introduction to the catalyst mass, (3) the temperature of the gas at that point, (4) the pressure of the gas, (5) the velocity of the gas in the catalyst zone, and (6) the heat distribution within the catalyst. For a given catalyst and gas composition the first two variables are fixed while the following

three can be determined arbitrarily, leaving only the sixth one beyond direct control. Obviously the heat distribution within the catalyst mass depends both on the amount of heat developed by the exothermic reaction in question and upon the rate of dissipation of this heat.

While the heat developed varies with the activity of the catalyst, the rate of heat removal depends only upon the arrangement of the catalyst chamber. The consequence is that two experiments, made with the same apparatus and under the same conditions with two catalysts of different activities, have different rates of heat transmission, and for that reason are not strictly comparable with each other. It is therefore necessary, if the results obtained are to have any meaning, to reduce to a minimum the effect of the variations in the rate of heat transfer between the catalyst mass and the surrounding medium for different experiments. In order to secure operating conditions as nearly isothermal as possible, the following three precautions were resorted to, with the result that the temperature difference between various points in the catalyst bed was kept within 5° C.

First, the gas mixtures employed contained carbon monoxide and hydrogen in the ratio 1:5, rather than in the theoretical ratio 1:2, thereby utilizing the diluent effect of the excess hydrogen to keep the temperature down. Second, the space velocity was regulated so as to give a low value for the heat liberated per second per cubic centimeter of catalyst. Since a pressure of 150 atmospheres was consistently employed, the adopted space velocity of 5000 corresponded to a time of contact of 28 seconds at 250° C. and 23.5 seconds at 350° C. Third, the apparatus was constructed in a form which insured the most rapid dissipation of heat from the catalyst bed. To accomplish this the catalyst was placed in a thin-walled tube of small diameter provided with a large number of longitudinal flanges. The catalyst tube, which had a capacity of only 15 cc., was then placed inside a high-pressure chamber of about 2000 cc. volume, maintained at a gas pressure of 150 atmospheres. By this arrangement the catalyst tube was intimately in contact with a gas volume, the specific heat of which was about 45 gram-calories, or more than ten times the amount of heat set free per second in the catalyst zone.

Apparatus

The apparatus is illustrated diagrammatically in Figure 2. The high-pressure chamber, E , capable of withstanding the working pressure, is heated externally by an electric resistance wire. The axial tube, T , is of small diameter with large contact surface, and holds the catalyst in position by

¹ Received January 19, 1928. We are indebted to Per K. Frolich and H. C. Hetherington for valuable assistance in translating and abstracting this article. The present paper is the first of a series presenting the results obtained in this study.

two transversal wire nets. A capillary metal tube, *C*, contains the thermocouple for temperature measurements at different points in the catalyst bed, the readings being recorded continuously. Compressed gas from the storage tank passes through the control valve, *V*₁, the gas meter, *C*₁, the recording pressure gage, *M*, and then enters the annular space between the jacket *E* and the tube *T*. After passing over the catalyst the gas leaves through the tube, *B*, passes

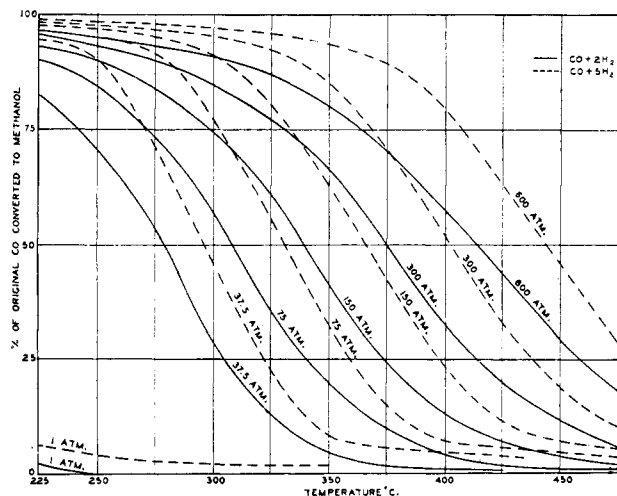


Figure 1—Per Cent Carbon Monoxide Converted to Methanol at Equilibrium for Two Gas Mixtures at Various Pressures and Temperatures

through the condenser, *R*, and escapes through the valve, *B*₂, after separation of the liquid methanol in the chamber, *S*.

Figure 3 shows from left to right the electrically heated chamber, *E*, the thermocouple tube, *C*, the catalyst tube, *T*, with radial flanges, the condenser, *R*, and the separator, *S*. In Figure 4 is shown a set of reactors and in Figure 5 the corresponding condensers and separators.

Preparation of Gas Mixtures

To avoid catalyst poisoning electrolytic hydrogen was used. The carbon monoxide, which was prepared by dehydration of formic acid with sulfuric acid, was treated with a solution of sodium hydroxide in vertical tubes filled with Raschig rings to remove vapors of formic acid and any sulfur-containing compounds which might have resulted from reduction of the sulfuric acid. Owing to the sensitivity of methanol catalysts to poisoning by iron carbonyl, precautions were taken to line all steel parts of the apparatus with some other metal. Furthermore, the gas mixtures were always carefully purified before entering the reaction chamber.

Method of Preparing Catalysts

From information contained in Sabatier's treatise on "Catalysis in Organic Chemistry" as well as from the present observations, it was apparent that the highest activity was obtained when the catalyst was prepared at low temperature. The various oxides investigated were therefore subjected to a reducing atmosphere at comparatively low temperatures. A slow current of hydrogen, at times charged with methanol (methanol was used in the reduction of the oxides of molybdenum, vanadium, tungsten, titanium, and uranium), was passed over the catalyst, the temperature being maintained at 200° C. during the first 4 hours and at 300° C. during the next 14 hours. When the catalysts were prepared by the wet method, the hydroxides were dried to constant weight in an oven at 110° C. before reduction.

Since the time of contact between the gas and the catalyst

for a constant inlet rate of flow depends upon the porosity of the contact mass, efforts were made to prepare the different catalysts in the form of grains of substantially the same shape and dimensions. To this end the hydroxides, etc., from which the catalysts were prepared, were pressed in the form of a paste through a die of 1.5 mm. diameter. The filaments thus obtained were dried and broken into fragments about 1.5 to 3 mm. long.

CATALYST STUDIES

In choosing catalysts for the synthesis of methanol it was desirable to start by determining the properties of those substances which Sabatier had found to be capable of decomposing methanol at atmospheric pressure into carbon monoxide and hydrogen. These substances were copper, cobalt, iron, platinum, nickel, and palladium, as well as certain metallic oxides. The results obtained with these and other catalysts are presented in the following:

Inert Oxides

Not even the slightest trace of methanol was formed with any of the following eleven oxides: alumina, silica, molybdenum oxide (Mo_2O_3), vanadium oxide (V_2O_5), blue tungsten oxide (W_2O_5), thoria, titanium oxide (TiO_2), magnesia, lime, barium oxide, and strontium oxide. Most of these substances as prepared—especially alumina, silica, thoria, titanium oxide, magnesia, and lime—had a composition between that of the hydrates from which they were derived and that of the anhydrous oxides obtained by prolonged calcination at higher temperature.

Active Oxides

Seven other oxides investigated were more or less active, the efficiency—that is, per cent of the entering carbon monoxide converted to methanol at 150 atmospheres and a space velocity of 5000—of the following four being less than 2 per cent: cerous oxide (Ce_2O_3), black uranium dioxide (UO_2), beryllium oxide (BeO), and zirconium oxide (ZrO_2). The three other oxides studied were manganous oxide (877), chromium sesquioxide (878), and zinc oxide (856), prepared by precipitation of the hydrates from the corresponding nitrates by means of sodium hydroxide. Comparative conversion figures for these three catalysts are given in Table I.

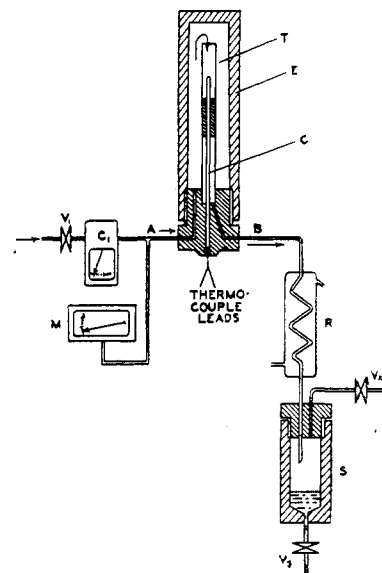


Figure 2—Diagram of Apparatus

TEMPERATURE ° C.	CATALYST 856 ZnO Per cent	CATALYST 877 MnO Per cent	CATALYST 876 Cr ₂ O ₃ Per cent
325	12	...	...
350	17.5	...	...
375	16	2	2
400	11.7	4	3.8
425	...	2.5	5
460	4.8	...	3.6

The activities of the catalysts are not, however, determined solely by their chemical composition. Thus, a brand

of commercial zinc oxide had an activity comparing closely with that of chromium sesquioxide—i. e., much lower than that of the zinc oxide listed in column 1 of Table I. This low activity persisted even after the zinc oxide had been dissolved in pure nitric acid, reprecipitated with sodium hydroxide, dehydrated, and reduced by the regular method.

Metallic Copper

As has already been pointed out by Sabatier, the properties of copper catalysts are profoundly influenced by the method of preparation. In general, active copper can be prepared only by reduction of the oxide, and it is essential that the temperature of reduction be kept at a minimum, since under otherwise constant conditions the activity of the resulting copper varies inversely with the temperature developed during reduction. Hence, in preparing the various copper catalysts described below, care was taken to prevent the temperature from rising above 250° C. The results show some rather remarkable relationships between the methods of preparation and the activities of the resulting catalysts.

HYDRATED CUPRIC OXIDE—When a solution of alkali hydroxide is added to a boiling solution of copper nitrate a black precipitate is formed, commonly called "tetra cupric hydrate" and corresponding to the formula $4\text{CuO} \cdot \text{H}_2\text{O}$. By reduction of the precipitate with hydrogen, Sabatier obtained a copper of low density and purplish color, characterized by high catalytic activity, and capable of decomposing methanol into carbon monoxide and hydrogen at atmospheric pressure. When the alkali-precipitated hydrate is heated above 300° C., it undergoes a transformation accompanied by a change in color and density. If, however, the temperature is kept below 300° C., the tetra cupric hydrate loses water gradually and is finally converted to anhydrous cupric oxide without any change whatever in appearance, apparent density, or temperature at which it starts to reduce.

These observations did not leave much evidence in favor of the assumption of a definite compound, and it was deemed desirable to compare the activity of the

the variation in weight must be taken into consideration. Thus, it is apparent that the conversions realized with catalysts 713 and 717 are roughly proportional to their weights.

However, the fact that the efficiencies of the two other catalysts, 715 and 716, are about 30 per cent higher than 713 and 717 on a weight basis, points to the necessity of employing low-temperature dehydration of the cupric hydrate.

FUSED CUPRIC OXIDE
—The reduction of fused cupric oxide

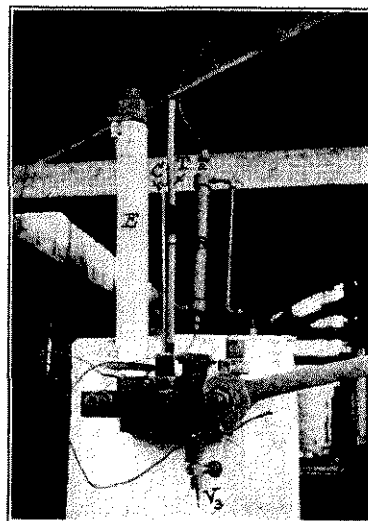


Figure 3—Main Parts of Apparatus

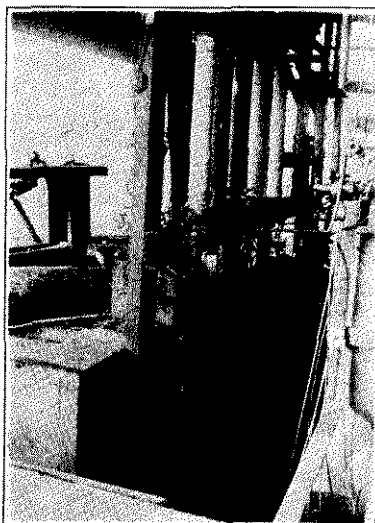


Figure 4—Battery of Reaction Chambers

yielded a catalyst, 821, whose properties differed decidedly from those just described. Its activity was perceptibly lower with a maximum conversion of only about 3 per cent, as seen from Figure 6.

CUPRIC OXIDE FROM CALCINATION OF ORGANIC SALTS—As might be expected, the oxides obtained by decomposition at low temperature of the unstable organic salts, such as the formate and acetate, give catalysts of approximately the same activity as those prepared by reduction of tetra cupric hydrate.

CUPROUS OXIDE—Cuprous oxide, which may be considered an intermediate step in the reduction of cupric oxide, was prepared by treatment of freshly reduced copper with nitrogen peroxide at 210–220° C. (Sabatier). The reduction of this compound with hydrogen resulted in a catalyst of considerable activity, 726 in Figure 6. Recalculated on a weight basis, however, the conversion falls in between

the catalysts prepared from tetra cupric hydrate.

catalysts produced under varying conditions of dehydration. A portion of the alkali-precipitated cupric hydrate, washed with distilled water until neutral to phenolphthalein, was therefore divided into four portions and heated to various temperatures for a period of 3 to 4 hours prior to reduction. The data for these catalysts, given in Table II and Figure 6, show some variation in the percentage of carbon monoxide converted to methanol. Since the catalyst volume was kept constant, however,



Figure 5—Condensers and Receivers for Reaction Chambers in Figure 4

CATALYST	TEMPERATURE OF HEAT TREATMENT ° C.	LOAD DENSITY	WEIGHT OF CATALYST USED Gram	OPTIMUM Temperature ° C.	ACTIVITY CO converted Per cent
713	100	0.90	0.680	387	21.8
716	200	0.90	0.720	365	32.8
715	270	0.90	0.720	370	30.0
717	700	1.21	0.967	365	32.8

CUPRIC OXIDE PRECIPITATED FROM CHLORIDE OR SULFATE SOLUTION—Entirely inactive metal was obtained by reduction of the oxides precipitated by alkali from boiling solutions of the chloride or sulfate. This is probably due to the poisoning effect of the adsorbed anion.

CUPRIC OXIDE PRECIPITATED FROM NITRATE SOLUTION IN THE COLD—In concluding the investigation of copper, a study was made of the properties of catalysts prepared from oxide precipitated with ammonia from a cold nitrate solution. The fact that this metal was completely inactive pointed to a promoter action of traces of alkali adsorbed on the tetra cupric hydrate catalysts described above. However, extensive experiments involving various degrees of washing

and addition of alkali to ammonia-precipitated catalysts proved beyond doubt that there was no connection between activity and alkali content, and hence it is impossible to

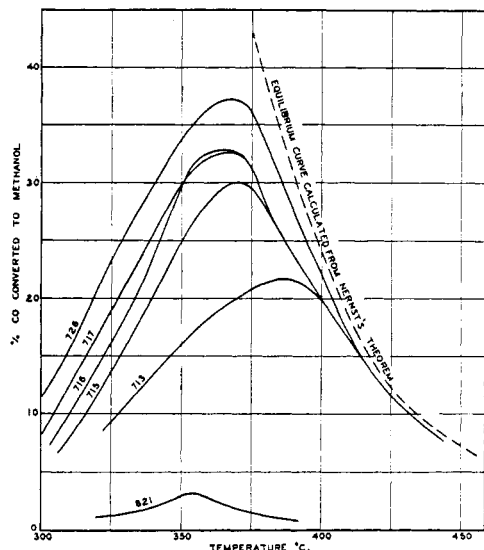


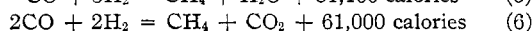
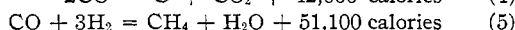
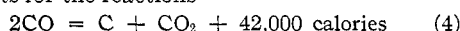
Figure 6—Efficiencies of Various Copper Catalysts Prepared by Different Methods

explain the differences observed between the two types of precipitates.

SUMMARY OF STUDIES ON COPPER—It is apparent that cuprous and cupric oxides give active catalysts by reduction with hydrogen. The method of preparing the oxides is important, however, and it is essential that the reduction be carried out at low temperature.

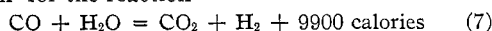
Metals Other than Copper

The metals iron, cobalt, nickel, platinum, and palladium, which all decompose methanol at atmospheric pressure, may a priori be expected to catalyze the reverse reaction—i. e., the high-pressure synthesis of methanol. However, these metals are also catalysts for the reactions



which all go with a decrease in volume, and hence methanol production is always accompanied by the formation of varying amounts of elementary carbon, carbon dioxide, and methane. Thus, the percentage of carbon monoxide converted to methanol by nickel is practically negligible compared with that entering into the above side reactions. This result is not surprising in view of the fact that the equilibrium conditions are considerably more favorable to methane production than to the formation of methanol.

By the application of Nernst's theorem and the equilibrium data of Hahn² for the reaction



it may be shown that methane and water predominate at equilibrium at the pressure here employed (150 atmospheres) as long as the temperature does not exceed 700° C. In other words, reaction (5) is favored thermodynamically, leaving practically no room for carbon dioxide at equilibrium under the conditions of the experiment. Nevertheless, it was found that carbon dioxide resulted when reduced (or perhaps only partly reduced) iron was used as the catalyst at 150 atmospheres and temperatures below 700° C. with a gas mixture containing carbon monoxide and hydrogen in the ratio 1:5. Undoubtedly, therefore, reaction (6) must

² *Z. physik. Chem.*, **42**, 705 (1908).

have taken place. It is impossible to say, however, whether the water vapor simultaneously formed resulted from reaction (5), or whether it was produced by interaction of the initially formed carbon dioxide with hydrogen by reversal of reaction (7).

Effect of Heat on Activity of Methanol Catalysts

From a commercial point of view the sensitivity of a catalyst to heat is a most important factor. It is well known that such metals as nickel, iron, cobalt, platinum, palladium, and copper lose their activity as hydrogenation catalysts when subjected to prolonged heating at sufficiently high temperature,³ and hence it was deemed desirable to study the effect of temperature on the activity of the methanol catalysts discussed above.

In general, the decrease in activity of copper catalysts is very pronounced when they are heated above the operating temperature. This loss in activity is most marked at the beginning of the heat treatment, the effect of prolonged heating being progressively less. Thus, preheating a copper catalyst promoted with cerium oxide to 450° C. for 1 hour in an atmosphere of hydrogen reduced the rate of methanol production by about 45 per cent, while the corresponding drop resulting from 22 hours' heating was about 60 per cent.

Identical heat treatment of the copper catalysts in Table II and Figure 6 demonstrated that the sensitivity to heat is influenced by the method of preparation of the catalysts, although it is impossible to lay down any simple rule for this relation. Furthermore, the higher the temperature to which the catalyst is raised, the greater the loss in activity, as would be expected.

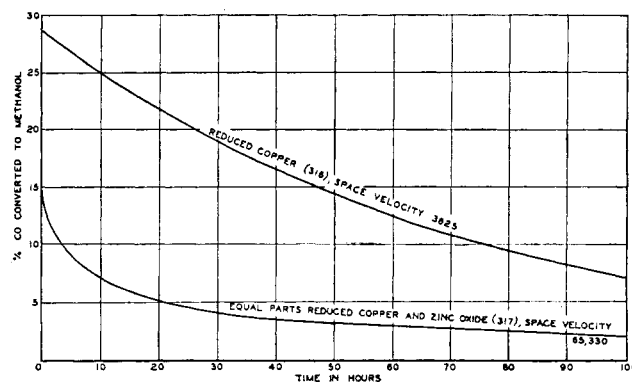


Figure 7—Decrease in Catalyst Activity as a Function of Time of Operation

Zinc oxide shows the same general behavior as copper, except that it is somewhat more sensitive to heat. This may be seen from the comparable data for zinc oxide and reduced copper in Table III.

Table III—Decrease in Catalyst Activity on Preheating

TREATMENT	CARBON MONOXIDE CONVERTED TO METHANOL	
	Reduced copper (713)	Zinc oxide (856)
	Per cent	Per cent
No preheating	21.8	17.9
Preheated for 6 hours at 450° C.	17.0 = 21.8 × 0.73	13.0 = 17.9 × 0.72
Preheated for 6 hours at 550° C.	14.2 = 21.8 × 0.65	7.7 = 17.9 × 0.43

In this respect the properties of manganous oxide and chromium sesquioxide are analogous to that of zinc oxide.

From these results it might be expected that the catalysts would show a progressive loss in activity in ordinary operation, and also that the effect would be the more marked the

³ This subject is reviewed in the reports of the Committee on Contact Catalysis with special reference to the work of Pease, *J. Am. Chem. Soc.*, **45**, 1196, 2235 (1923).

higher the temperature of operation. That this is actually the case is brought out by numerous experiments, of which two striking examples are given in Figure 7. In these two runs the experimental conditions were purposely chosen in order to permit superheating of the catalyst mass. The rigorous purification employed excluded any poisoning effect.

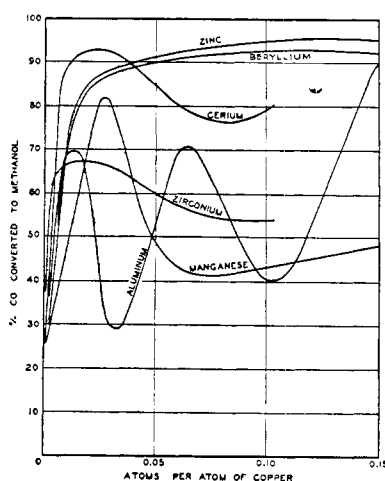


Figure 8—Maximum Activity of Promoted Copper Catalysts

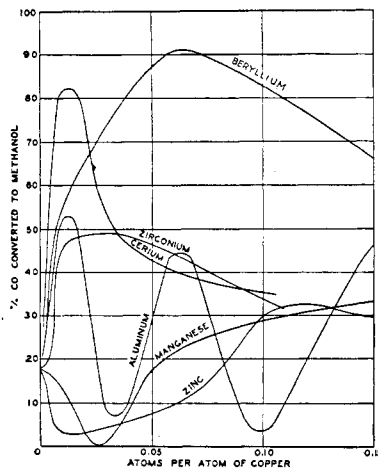


Figure 9—Maximum Activity of Promoted Copper Catalysts Shown in Figure 8 after Heat Treatment (Exposure to Hydrogen for 6 Hours at 450° C.)

Catalytic Properties of Mixtures

Numerous examples are known of reactions whose rates are enormously increased by catalysts composed of mixtures of which one or more components are active when used alone. In studying the effect of such mixtures on the methanol reaction, reduced copper was chosen as the basic constituent, since the previous experiments had shown it to be the most active single catalyst. In the systematic investigation made, a large variety of substances were added to copper and activity tests made for each mixture. While it may be objected that this is an empirical method of attack and that one is liable to leave unexplored some particular mixture of outstanding activity, it is nevertheless the only means of pursuing a search for catalysts for a specific reaction. Only by the assembling of accurate and extended experimental data is it possible to accumulate results for inspiration of fertile hypotheses.

A few of the results obtained in the course of this work are presented below. All catalysts were prepared by precipitation of the hydroxides from the mixed nitrate solutions with a boiling solution of sodium hydroxide. As before, a gas mixture containing carbon monoxide and hydrogen in the ratio 1:5 was used at a pressure of 150 atmospheres and a space velocity of 5000. For all mixtures the sensitivity to heat was determined by preheating separate samples of the reduced catalyst to 450° C. for 6 hours in an atmosphere of hydrogen.

COPPER AND ZINC OXIDE—The results obtained with mixtures of copper and zinc oxide are given in Table IV. It is apparent that the initial activity of copper is markedly increased by the addition of relatively small amounts of zinc oxide, but the catalyst mixtures are still sensitive to heat, as is most clearly brought out by the corresponding curves in Figures 8 and 9.

COPPER AND MANGANOUS OXIDE—The data in Table V show a rapid increase in activity for small additions of manganous oxide with a maximum at a Mn-Cu ratio approximating 3:100. Further amounts of manganous oxide decrease the activity, which reaches a minimum at a ratio of about 15:100, followed by a gradual increase to a value somewhat lower than the original maximum. It is also

interesting to note that the catalyst possessing maximum activity is most sensitive to heat, while subsequent additions of manganous oxide make it considerably more resistant.

COPPER, MANGANOUS OXIDE, AND CHROMIUM SESQUIOXIDE—The results obtained with copper and manganous oxide suggested the addition of a third compound to the two mixtures which possessed the maximum activity without and with preheating—viz., Mn-Cu = 3:100 and 37.5:100. Chromium sesquioxide was chosen for this purpose.

From Figure 10 it will be seen that the addition of chromium sesquioxide to the mixture low in manganous oxide yields catalysts of high activity and considerable resistance to heat. The mixtures of high manganous oxide content have even higher initial activity and are also rendered less sensitive to heat by increasing amounts of chromium sesquioxide.

COPPER, MANGANOUS OXIDE, AND BERYLLIUM OXIDE—The substitution of beryllium for chromium in the preceding mixtures gave less active catalysts, showing that chromium sesquioxide is preferable.

COPPER AND ALUMINA—Mixtures of copper and alumina give irregular activity curves with several maxima and minima. The highest efficiency is obtained with an Al-Cu ratio of 15:100, corresponding to 90 per cent conversion of the entering carbon monoxide. The resistance to heat is also variable and not very high, the two activity curves being of the same general form (Figures 8 and 9).

COPPER AND ZIRCONIUM OXIDE—The addition of zirconium oxide to copper fails to bring the conversion above 67 per cent, a value which must be considered low compared with some of the other mixtures investigated.

CATALYST	ATOMS Zn PER ATOM Cu	MAXIMUM PER CENT CO TO METHANOL			
		UNTREATED	° C.	PREHEATED	° C.
713	0.00	21.8	385	17.0	385
860	0.01	72.5	290	3.0	420
861	0.03	89.0	285	4.5	390
862	0.06	91.0	280	9.0	380
863	0.10	95.0	275	30.0	345
864	0.15	95.0	265	28.0	350

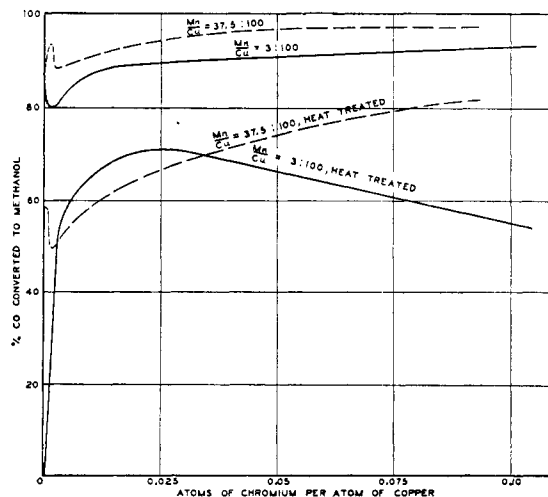


Figure 10—Efficiency of Mixed Catalysts Consisting of Copper, Manganese, and Chromium

COPPER AND CERIUM OXIDE—Small amounts of cerium oxide have a marked effect on copper. A maximum is reached at a Ce-Cu ratio of about 30:100 with 92 per cent of

the entering carbon monoxide being converted to methanol. The catalysts low in cerium oxide possess marked resistance to heat, giving a maximum conversion of 82 per cent, but lose this property very rapidly for Ce-Cu ratios above 10:100.

Table V—Copper-Manganese Oxide Catalysts

Catalyst	Atoms Mn per Atom Cu	Load Density	Maximum Per Cent CO to Methanol			
			Untreated		Preheated	
			% Con- version	° C.	% Con- version	° C.
713	0.0900	0.90	21.8	387	17.0	385
725	0.0050	0.96	44.3	348	16.7	390
724	0.0125	1.03	49.3	345	14.2	395
723	0.0250	0.87	81.6	333	0.0	377
722	0.0500	0.93	48.7	348	18.0	377
721	0.1250	0.90	46.7	342	31.3	362
720	0.2500	0.84	56.7	345	39.3	360
719	0.3750	0.87	70.6	315	62.0	338
718	0.5000	0.97	76.0	265	56.4	315
615	1.0000	1.03	78.0	330	51.0	352

COPPER AND BERYLLIUM OXIDE—Besides increasing the initial activity, additions of beryllium have the advantage of yielding the most heat-resistant catalysts of this whole series, as is brought out by the curves in Figures 8 and 9, showing a maximum conversion of about 91 per cent for the heat-treated mixture of Be-Cu ratio 6:100.

Summary and Conclusions

From the results presented in this paper it is apparent that a number of substances which decompose methanol at elevated temperature and atmospheric pressure are capable of catalyz-

ing the synthesis of the alcohol by the reverse reaction using carbon monoxide and hydrogen at high pressure.

Reduced copper and zinc oxide are the most active of the methanol catalysts studied. Manganous oxide and chromium sesquioxide are of a considerably lower order, and the remaining oxides are too inactive to consider it worth while to employ them alone.

The method of preparing the catalysts is of utmost importance. This has been brought out particularly by the extensive studies of copper, showing that cuprous and cupric oxides give active catalysts with reduction by hydrogen, when prepared by precipitation of the nitrate or by thermal decomposition of the unstable copper salts of organic acids. It is essential that the reduction be carried out at low temperature. Copper catalysts prepared from the hydroxide precipitated from solutions of the sulfate and chloride are entirely inactive.

All of these single-component catalysts are very sensitive to heat, as has been brought out by the lowering in methanol conversion resulting from heat treatment somewhat above the temperature of operation.

In general, mixed catalysts are superior to single-component catalysts, as manifested both by the great increase in the rate of methanol production and by the greater resistance to heat.

In regard to the behavior of mixed catalysts, the material here presented does not permit of any definite conclusions. The data plotted for a large variety of such mixtures in Figures 8 and 9 are too erratic for a simple interpretation.

Comparative Study of Values Obtained in Synthesis of Methanol^{1,2}

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THE writers have found it interesting to make a comparative study of the values obtained in the work of Audibert and Raineau³ with their own and that recently published by Lewis and Frolich.⁴ In this they have limited themselves to one temperature, 400° C., for which their results have been published.⁵

Audibert and Raineau have employed the Nernst approximation formula in a form involving the total pressure under which the reaction is carried out. The development for the methanol reaction of this form of that equation is the following:

For the reaction

$$\text{CO} + 2\text{H}_2 = \text{CH}_3\text{OH} + Q \text{ calories} \quad (1)$$
 we have after Nernst

$$\log K^1_p = \frac{-Q}{4.571 T} + \Sigma v 1.75 \log T + \Sigma v C \quad (2)$$

Now if x represents the mol fraction of carbon monoxide converted to methanol and P represents the total pressure in atmospheres, then

$$K^1_p = \frac{[P_{\text{CO}}][P_{\text{H}_2}]^2}{[P_{\text{MeOH}}]} = \frac{P(1-x)}{3-2x} \frac{4P^2(1-x)^2}{(3-2x)^2} \frac{1}{3-2x} = \frac{4P^2(1-x)^3}{x(3-2x)^2}$$

$$\text{also } \log K^1_p = \log \frac{(1-x)^3}{x(3-2x)^2} + 2 \log P + \log 4$$

$$\text{and (2) becomes } \log \frac{(1-x)^3}{x(3-2x)^2} = \frac{-Q}{4.571 T} + \Sigma v 1.75 \log T + \Sigma v C - 2 \log P - \log 4.0$$

For the methanol reaction (1) we have this approximation:

$$\log \frac{(1-x)^3}{x(3-2x)^2} = \frac{-Q}{4.571 T} + 3.5 \log T + 2.99794 - 2 \log P \quad (3)$$

$$\text{since } \Sigma v C - \log 4 = 3.5 + (2 \times 1.6) - 3.1 - 0.60206 = 2.99794$$

Per Cent Conversions

Without entering into the accuracy of this method of calculation and accepting it as a suitable or even empirical representation of the conversions approached experimentally by Audibert and Raineau, the writers have made comparisons of their per cent conversions at 400° C. with those of other recently published work. Of these, Audibert and Raineau employed a very active catalyst and a medium space velocity of 5000; Lewis and Frolich term their catalyst as one of medium activity, and for comparison we have selected from their published results the maximum experimental value⁶ for their conversion at 400° C., namely, 26 per cent at a space velocity of about 625; Brown and Galloway used an active

¹ Received July 7, 1928.

² Since this discussion was written, the report of Morgan, Taylor, and Hedley in *J. Soc. Chem. Ind.*, 47, 117T (1928), has appeared. Their preliminary results on the methanol equilibrium under pressure are in close agreement with the Nernst approximation values of Audibert and hence with the maximum experimental values of this discussion. They have also found normal zinc chromate to be a very active catalyst and in agreement with Brown and Galloway more active than the basic chromate at high temperatures.

³ Page 1105, this issue.

⁴ *IND. ENG. CHEM.*, 20, 285 (1928).

⁵ *Ibid.*, 20, 960 (1928).

⁶ See Figure 5 of reference 2.